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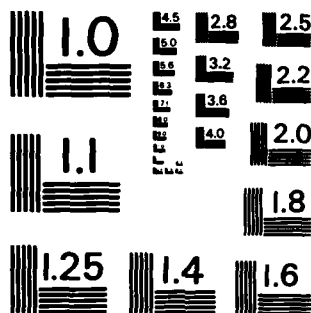UNCLASSIFIED    20 NOV 84 TR-12 N00014-77-C-0376           F/G 11/9     NL

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We studied the effect of deuteration of polystyrene on the miscibility behavior of polystyrene-polybutadiene blend systems.  We prepared a polystyrene having its aromatic hydrogens replaced by deuterium by starting from an ordinary polystyrene and treating it with deuterated benzene in the presence of an organometallic catalyst.  We also prepared, as a control, a hydrogeneous polystyrene of closely similar structure by repeating the same procedure except that this time ordinary, rather than deuterated,

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benzene was used. These matching pairs of hydrogeneous and deutereous
polystyrenes, when mixed with a polybutadiene or a styrene-butadiene
random copolymer, were shown to give practically identical cloud point
curves, thus indicating that the deuterium isotope effect is negligible.

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TECHNICAL REPORT NO. 12


Deuterium Isotope Effect on the Compatibility

between Polystyrene and Polybutadiene


by


J. L. Lin, D. Rigby and R. J. Roe


Prepared for Publication

in

Macromolecules


Department of Materials Science
and Metallurgical Engineering
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# INTRODUCTION

The availability of small-angle neutron scattering techniques in recent years has opened up many new avenues of research in polymer field. In neutron scattering studies deuterated polymer molecules are often substituted for some of the usual, hydrogeneous molecules as a means of selective labeling. Such substitution relies on the fact that the neutron scattering lengths of deuterium and hydrogen are very different, while the difference in other physical and chemical properties between the deuterated and hydrogenated counterparts is usually negligibly small. In some cases, however, the properties differ significantly enough to produce measurable isotope effects. For example, the difference in the melting points between polyethylene and deuterated polyethylene leads to the clustering of the latter in the crystals obtained from a mixture.[1,2] The theta temperature of polystyrene in cyclohexane is altered when either the polymer or the solvent is deuterated.[3] In the study of polymer blends, the compatibility of polystyrene/polybutadiene and polystyrene/poly(vinyl methyl ether)[5] blend systems appears to be modified when the polystyrene is substituted by its deuterated equivalents.

In this work we re-examine the question of deuterium isotope effect on the polymer blend compatibility. We have prepared pairs of hydrogenated and deuterated polystyrenes of closely similar structure and molecular weight distribution through a hydrogen (or deuterium) exchange[6,7] reaction, starting from the same batches of polystyrene samples. Compatibility of these

polymers with butadiene homopolymer or styrene-butadiene random copolymer was then studied by means of cloud point measurements.

EXPERIMENTAL

Two anionically-polymerized polystyrenes, obtained from the Pressure Chemical Company, were used as the starting material for the exchange reaction. These two polystyrenes, having the nominal molecular weights of 2,000 and 100,000 are given the designation 2KPS and 100KPS, respectively. The aromatic hydrogens of polystyrene can be exchanged to deuteriums by reacting the polystyrene with excess deuterated benzene in the presence of an organometallic catalyst.[6,7] The procedure we used is briefly as followed: to the solution of 2g of polystyrene dissolved in 20g of $C_6D_6$ we added 0.18ml of the catalyst, ethylaluminium dichloride and a small amount of HCl gas as a co-catalyst. After four hours of gentle agitation under nitrogen in a shaker, the catalyst was destroyed with water, and the polymer was isolated and dried. The deuterated samples are designated 2KPSD and 100KPSD, respectively, depending on the starting material. Their extents of deuteration were determined by NMR and were found to be 93.3% and 93.8% of aromatic hydrogens, respectively. Next, the same reaction was repeated under exactly the same conditions but this time with ordinary benzene instead of deuterated benzene. The polystyrenes thus obtained, in which the aromatic hydrogens were replaced by other hydrogen atoms from the benzene, are designated 2KPSH and 100KPSH. These two hydrogeneous polystyrenes were prepared as a

"control"; that is, for the purpose of comparison with the behavior of the deuterated polystyrenes. The above-mentioned hydrogen-exchange reaction is evidently accompanied by side reactions, chain scission and crosslinking (or chain grafting). After the reaction, the molecular weight of polystyrenes of initially fairly long chains was seen to decrease slightly, while that of initially short chains was seen to increase slightly.[6] By the above procedure of preparing the controls, we can be fairly sure of having matching pairs of hydrogeneous and deutereous polystyrenes of closely similar structure and molecular weight distribution.

The molecular weight distributions of all six polystyrene samples were determined with GPC and the average molecular weights calculated from the chromatograms are listed in Table I. All the samples were run on the same day one after the other, so that any error in the calibration would have affected all of them similarly.

For the miscibility studies, the 2000 MW polystyrenes were mixed with a polybutadiene, obtained from Goodyear Chemical Company, having $M_n$ by (VPO) of 2350 and $M_w/M_n$ ratio (by GPC) of 1.13. The 100,000 MW polystyrenes were mixed with styrene/butadiene random copolymer containing 68.4 weight % styrene. Its GPC characterization data are also listed in Table I. This copolymer was prepared by radical polymerization at 60°C in a mixed solvent containing benzene and ethylbenzene in the ratio of 1 to 4. The conversion was confined to about 10% (18 hours) in order to limit the compositional heterogeneity in the random copolymer molecules.

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The cloud points of the mixtures were determined by light scattering as described in our earlier publication.[8]

## RESULTS AND DISCUSSION

The cloud points determined with the series of mixtures containing the polybutadiene as the first component and one of the 2K polystyrenes as the second component are given in Figure 1. The two polystyrenes, 2KPSD and 2KPSH, which went through the exchange reaction, show about the same cloud point curves, which are clearly different from the cloud point curve obtained with the original, untreated polystyrene. Figure 2 shows the cloud points determined with the series of mixtures containing the styrene-butadiene random copolymer and one of the 100K polystyrenes. Here again, the two treated polystyrenes, 100KPSD and 100KPSH, give almost identical cloud point curves, whereas the cloud points obtained with the untreated polystyrene is displaced about 60° higher in temperature.

Table I shows that both 2KPSD and 2KPSH have higher MW than the original 2KPS, while 100KPSD and 100KPSH have lower MW than the original 100KPS. This is in accord with the results obtained by Willenberg,[6] and probably results from the fact that the effect of chain scission is more sensitively reflected in the average molecular weight of longer chains, whereas with short chains the chain grafting (or crosslinking) is the more important effect. As a consequence of these changes in the chain lengths, the cloud point curves have shifted upward in the case of 2K polystyrenes, but shifted downward in the case of 100K

polystyrenes. The direction of change is in agreement with the direction of change in the molecular weight. But the magnitudes of change are much higher than expected from the molecular weight changes alone. To see this, we make the following simple analysis.

We have shown earlier[8] that the miscibility behavior of polymer blends, in particular of those involving styrene and butadiene constituents, can be described *semi-quantitatively* on the basis of the Flory-Huggins free energy of mixing, which we write as

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln\phi_1 + (1/V_2)\phi_2 \ln\phi_2] + \Lambda\phi_1\phi_2 \qquad (1)$$

where $\Delta G_M$ is per unit volume of the mixture, $V_1, V_2$ are the molar volumes, $\phi_1, \phi_2$ are the volume fractions of the components, and $\Lambda$ is the interaction energy density. On the assumption that $\Lambda$ is independent of composition, the critical temperature $T_C$ can be derived from (1) as

$$T_C = (\Lambda/R)2V_1V_2/(\sqrt{V_1}+\sqrt{V_2})^2 . \qquad (2)$$

Taking component 1 as the polybutadiene or the styrene-butadiene random copolymer and component 2 as the polystyrene, we are interested in the variation in $T_C$ induced when $V_2$ is varied. By differentiating (2) (and neglecting the small temperature dependence[8] of $\Lambda$) we obtain

$$\partial \ln T_C/\partial \ln V_2 = 1/[1 + (V_2/V_1)^{1/2}] . \qquad (3)$$

For polydisperse polymers, the critical temperature is determined by the weight-average as well as the z-average molecular weights[9,10] (or the molar volumes). Since the polydispersity of our samples is fairly low, we will simply use

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the weight-averages and utilize eq. (3) to calculate the expected variation in $T_C$ induced by the changes in the molecular weight or $V_2$. For the 2K polystyrenes, the change in $M_w$ is 6.6%, which should have produced 3.3% or 13° increase in $T_C$, much smaller than the observed increase of about 17°. For the 100K polystyrenes, $M_w$ has decreased after the exchange reaction by 12.6%, which should have produced a decrease in $T_C$ of 2.9% or about 11° (note that $V_2/V_1$ is very large in this case). The observed decrease in $T_C$ is about 60°. The large discrepancy between the observed and expected change in $T_C$ suggests that the miscibility behavior of polymer blends is sensitive to the fine structure of the polymers such as the degree of branching or possibly the tacticity, in addition to the molecular weight and molecular weight distribution. Our results, on the other hand, suggest that the deuterium isotope effect is negligible at least in the styrene-butadiene system we studied.

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## Table I
## Characterization of Polymer Samples

| Sample | Remarks | $M_n$ | $M_w$ | $M_z$ |
|---|---|---|---|---|
| 2KPS | Pressure Chemical Co. Untreated | $1.75 \times 10^3$ | $1.96 \times 10^3$ | $2.16 \times 10$ |
| 2KPSD | Deuterated 93.3% D | 1.95 | 2.10 | 2.26 |
| 2KPSH | Hydrogen Exchanged | 1.94 | 2.08 | 2.23 |
| 100KPS | Pressure Chemical Co. Untreated | 95.4 | 101.7 | 107.9 |
| 100KPSD | Deuterated 93.8% D | 79.2 | 91.2 | 101.0 |
| 100KPSH | Hydrogen Exchanged | 72.7 | 91.4 | 103.8 |
| PBD | Goodyear Chemical Co. (CDS-B3) | 2.35 | 2.66 | --- |
| S/B random copolymer | 68.4% styrene | 4.56 | 8.58 | 17.5 |

LEGEND TO FIGURES

Figure 1.   Cloud points obtained with mixtures containing
polybutadiene ($M_n$ = 2350) as the first component and
one of the polystyrenes of approximately 2000
molecular weight as the second component. Triangles:
2KPS, ordinary polystyrene obtained from Pressure
Chemical Company. Open circles: 2KPSD, deuterated
polystyrene prepared by treating 2KPS polystyrene with
deuterated benzene. Closed circles: 2KPSH,
hydrogeneous polystyrene prepared as a control by
treating 2KPS polystyrene with ordinary benzene.

Figure 2.   Cloud points obtained with mixtures containing
styrene-butadiene random copolymer ($M_w$ = 8600, styrene
68.4%) as the first component and one of the
polystyrenes of approximately 100,000 molecular weight
as the second component. Triangles: 100KPS, ordinary
polystyrene obtained from Pressure Chemical Company.
Open circles: 100KPSD, deuterated polystyrene
prepared by treating 100KPS polystyrene with
deuterated benzene. Closed circles: 100KPSH, a
control prepared by treating 100KPS polystyrene with
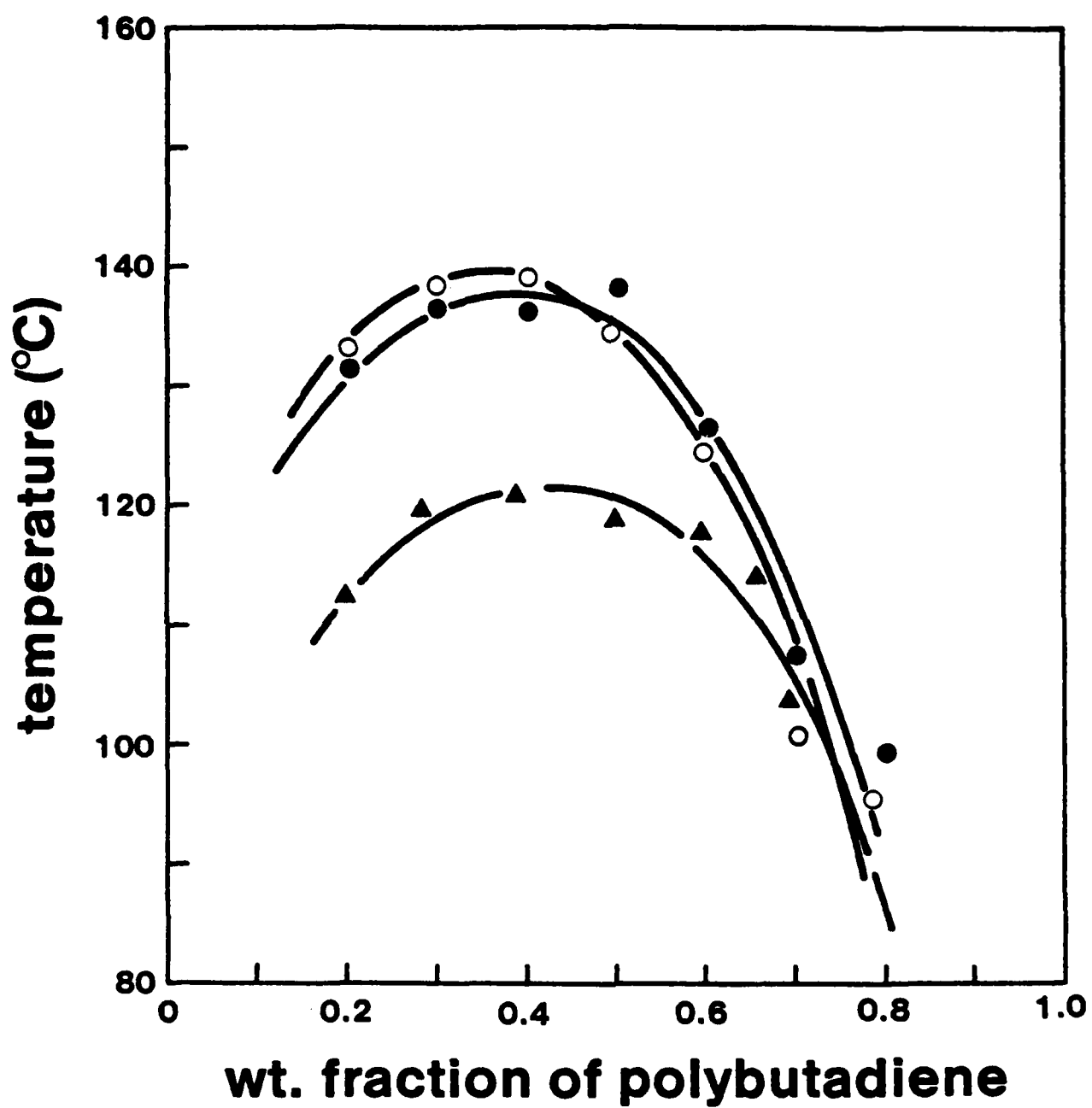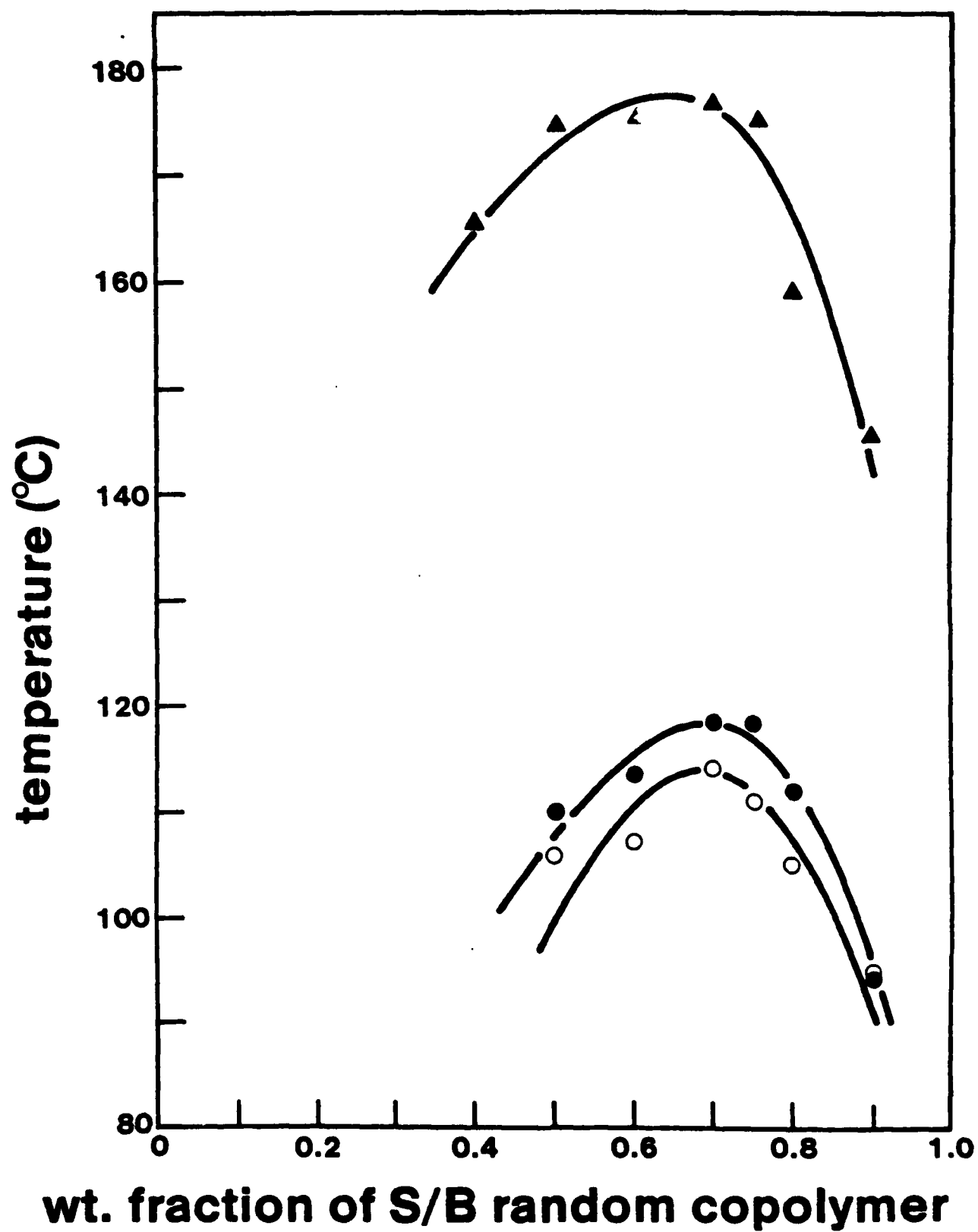ordinary benzene.

FIGURE 1

FIGURE 2

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